

ANALYSIS OF GASES IN METALS

by
Z. M. Turovtseva and L. L. Kunin

Authorized translation from the Russian
by James Thompson, B.Sc. (Hons.)



CONSULTANTS BUREAU
NEW YORK

The original Russian text
was published by the
Publishing House of the Academy of Sciences
of the USSR in
Moscow and Leningrad in 1959
for the V. I. Vernadskii Institute
of Geochemistry and Analytical Chemistry.

Зинаида Михайловна Туровцева
и Лев Лазаревич Кунин

АНАЛИЗ ГАЗОВ В МЕТАЛЛАХ

Library of Congress Catalog Card Number: 61-10018
Copyright 1961 Consultants Bureau Enterprises, Inc.
227 West 17th St., New York 11, N. Y.
All rights reserved

*No part of this publication may be reproduced
in any form without written permission
from the publisher*

Printed in the United States of America

PREFACE

The effect of small amounts of impurities of hydrogen, oxygen and nitrogen on the properties of metals and alloys was first discovered in the last century.

The first investigations on the hydrogen-iron system were carried out by Cailletet in 1864 and in the hydrogen-palladium system by Graham in 1866.

In 1882 Ledebur proposed the hydrogen method for determining oxygen in metals, which can also be adapted to determine hydrogen. The chemical method for determining nitrogen in metals, which has lost none of its importance, was proposed by Boussingault in 1850 and developed by Kjeldahl in 1883.

The analysis of gases in metals received its most intensive development in the 1920's from the work of Oberhoffer and also Jordan and Eckman; the result of this work is the vacuum-fusion method.

In the 1930's the Soviet investigators N. P. Chizhevskii and Yu. A. Klyachko carried out fundamental studies on the behavior of gases in steel and aluminum. It was at this time that methods for analyzing gases in metals were introduced in the scientific research institutes and certain plants. The first work in this field was closely tied up with investigations into, and the selection of, the best methods for extracting and processing metals.

In the postwar period, in connection with the development of new alloys and the preparation of pure metals, the analysis of gases in metals was widely developed.

In addition to modifications to existing methods, entirely new methods of analysis were developed and the apparatus was improved. Papers appeared dealing with the theoretical fundamentals in the analysis of gases in metals. Whereas once they were of interest only to highly specialized research workers, these methods of analysis were now used on a regular basis in plants and scientific research institutes.

The appearance in 1953 of the well-known book by Yu. A. Klyachko, A. G. Atlasov, and M. M. Shapiro "The Analysis of Gases and Inclusions in Steel" was an important stage in the development of

the field of analysis dealt with here. This book combined the results of Soviet and non-Soviet work, gave a number of definite recommendations for a wide circle of workers, and underlined the clear possibilities for further development in the analysis of gases in steel, ferroalloys, and certain pure metals.

Sloman (Britain), Mallett (USA), and other Soviet and non-Soviet workers have made important contributions to the development of the vacuum-fusion method. At the present time, this is the method used to analyze gases in practically all metals.

Only in recent years have modifications been proposed for the vacuum-fusion method in a graphite powder, in a platinum bath, and also fusion in a quartz crucible with tin to determine hydrogen, etc.

The conditions for the extraction of oxygen in the vacuum-fusion method were studied in relation to the form in which the oxygen was present (Yu. A. Klyachko, et al., N. F. Leve, B. A. Shmelev, Sloman, Harvey, and Kubaschewski), to the working of a blank bath, and the action of adsorption-active sublimates (Yu. A. Klyachko, et al., V. A. Zhabin, and Smith), and to a number of other factors. Fundamental work on the use of the vacuum-fusion method in the analysis of pure metals was carried out in the V.I. Vernadskii Institute of Geochemistry and Analytical Chemistry (GEOKhI).

Important advances have also been made in the design of apparatus for the vacuum-fusion method of analysis in the Institute of Metallurgy of the Academy of Sciences of the USSR (IMET), the Central Scientific Research Institute for Ferrous Metallurgy (TsNIChM), and in the Institute for Geochemistry and Analytical Chemistry (GEOKhI).

Important advances have been made not only in the vacuum-fusion method but also in the use of physical methods for analyzing gases in metals. In this connection, improvements have been made in the use of spectral analysis. In fact, some of the proposed methods only involve the spectral analysis of the extracted gas mixture. Of considerable interest is the work on the spectral analysis of gases in metals by discharge in a hollow cathode (Rosen). Important investigations on the development of this method for determining oxygen and nitrogen in steel were carried out by S. A. Mandel'shtam and O. B. Fal'kova; N. S. Sventitskii, et al. have made important contributions to the spectral determination of hydrogen in metals. Important advances have been made in the methods for determining gases in metals using stable isotopes followed by mass-spectrometric (Kirshenbaum) and spectral (A. N. Zaidel') determinations.

The sulfur (A. K. Babko) and bromine-carbon (Codell and Norwitz) methods for determining oxygen are very promising.

The extensive introduction of new methods of analysis for all metals, the appearance in the literature of papers with varying degrees of importance, and the accumulation of much operating experience have given rise to the need for a special book on the analysis of gases in metals.

This book deals with the theory of analysis and gives a description of the apparatus and methods as well as their application to the analysis of metals in all groups of the periodic system.

Chapter X on the analysis of nitrogen in metals by chemical methods was written by the late B. A. Generozov. This chapter has been included because these methods are fairly accurate for the determination of nitrogen. On the other hand, the vacuum-fusion method, which gives reliable results in the determination of hydrogen and oxygen, is sometimes unsuitable for the determination of nitrogen in metals.

CONTENTS

Part One. THEORETICAL PRINCIPLES IN THE DETERMINATION OF GASES IN METALS

Introduction	3
Chapter I. THE HYDROGEN—METAL SYSTEM	5
1. The Thermal Stability of Hydrogen—Metal Systems	5
2. Diffusion of Hydrogen in Metals	15
3. Time of Degassing and Amount of Hydrogen Evolved	19
4. Brief Characteristics of Methods for Determining Hydrogen in Metals	25
Chapter II. NITROGEN—METAL SYSTEMS	29
1. The Solubility of Nitrogen in Metals and the Thermal Stability of Nitrides	29
2. Brief Characteristics of Methods for Determining Nitrogen	37
Chapter III. OXYGEN AND METALS	43
1. Characteristics of the Solution of Oxygen and Oxidation of Metals ..	43
2. Characteristics of Methods for Determining Oxygen	52
Chapter IV. PHYSICOCHEMICAL PRINCIPLES IN THE DETERMINATION OF GASES IN METALS BY THE VACUUM-FUSION METHOD	79
1. Extraction of Gases	79
2. The Formation of Adsorption-Active Sublimates	84
3. Vapor Pressure of Metals	88
4. Distribution of Sublimate	97
5. Working Parameters of the Apparatus	103
Literature Cited	109

Part Two. METHODS OF ANALYSIS AND APPARATUS

Chapter V. APPARATUS FOR ANALYSIS OF GASES IN METALS BY THE VACUUM-FUSION METHOD	117
1. Extraction Part	117
2. System of Vacuum Pumps for Evacuating and Collecting Extracted Gases	123
3. Analytical Part	125
4. The Determination of Gases in Metals by the Vacuum-Fusion Method on the GEOKhI Apparatus	133

CONTENTS

Chapter VI. METHODS OF ANALYSIS BASED ON THE EXTRACTION OF OXYGEN INTO THE GASEOUS PHASE	145
1. Determining Gases in Metals by Fusion in an Argon Atmosphere. . .	145
2. Determining Oxygen in Metals by the Bromine—Carbon Method. . .	149
3. The Sulfur Method for Determining Oxygen in Metals	154
4. Determining Oxygen by the Hydrogen Method	158
Chapter VII. METHODS OF ANALYSIS BASED ON THE EVOLUTION OF OXYGEN PRESENT AS INCLUSIONS	163
1. Method of Mercury Extraction to Determine Oxygen in Metals . . .	163
2. Distillation Method	166
3. The Chlorination Method for Determining Oxygen in Metals	169
Chapter VIII. SPECTRAL METHODS FOR ANALYZING GASES IN METALS	171
1. Determining Gases in Metals Using Three Types of Spark	172
2. Determining Gases in Metals in a Direct-Current Arc.	178
3. Determining Gases in Metals in a Hollow Cathode.	184
4. Analyzing Gas Mixtures by Spectral Methods	187
Chapter IX. OTHER PHYSICAL METHODS FOR DETERMINING GASES IN METALS	193
1. Method of Isotopic Balancing for Determining Hydrogen in Metals .	193
2. The Method of Isotopic Dilution to Determine Oxygen in Metals. . .	194
3. A Radioactivation Method for Determining Oxygen in Metals.	198
4. The Use of X-ray Structural Analysis to Determine Gases in Metals	201
Chapter X. DETERMINING NITROGEN IN METALS BY CHEMICAL ANALYSIS	207
1. Decomposing Nitrides of Metals by Chemical Methods.	207
2. The Method for Decomposing Nitrides Developed in the Chemical Laboratory of the Central Scientific Research Institute for Ferrous Metallurgy (TsNIChM)	211
3. Distillation of Nitrogen (Ammonia).	213
4. Colorimetric Methods for Determining Nitrogen.	219
Literature Cited	225

Part Three. THE DETERMINATION OF GASES IN METALS ACCORDING TO THE GROUPS OF THE PERIODIC TABLE

Chapter XI. A COMPARATIVE EVALUATION OF ANALYTICAL METHODS	231
Chapter XII. DETERMINING GASES IN METALS OF THE FIRST GROUP	281
1. A Review of Methods Used for Analyzing Gases in Alkali Metals . .	281

CONTENTS

2. Determining Oxygen in Sodium and Potassium—Sodium Alloy by the Vacuum-Fusion Method	283
3. Determining Oxygen in Sodium and Potassium—Sodium Alloy by the Mercury-Extraction Method	287
4. Determining Nitrogen in Lithium	291
5. Determining Gases in Copper and Silver	291
Chapter XIII. DETERMINING GASES IN METALS OF THE SECOND GROUP	295
1. Determining Gases in Beryllium	295
2. Determining Oxygen in Magnesium and Calcium by the Distillation Method	300
3. Determining Oxygen in Calcium Using Absolute Methyl Alcohol . . .	307
4. Determining Oxygen in Zinc	310
Chapter XIV. DETERMINING GASES IN METALS OF THE THIRD GROUP	313
1. Determining Gases in Boron by the Vacuum-Fusion Method	313
2. Determining Gases in Aluminum	313
3. Determining Gases in Yttrium	316
Chapter XV. DETERMINING GASES IN METALS OF THE FOURTH GROUP	317
1. A Review of Methods Used for Determining Gases in Titanium and Zirconium	317
2. Determination of Hydrogen and Oxygen in Titanium and Zirconium by the Vacuum-Fusion Method Using an Iron Bath	319
3. Determining Gases in Titanium by the Vacuum-Fusion Method Using a Graphite Powder	323
4. The Determination of Hydrogen and Oxygen in Titanium Using Carbon Sleeves	325
5. The Determination of Oxygen and Hydrogen in Titanium and Zirconium by the Vacuum-Fusion Method with a Platinum Bath	326
6. Determination of Hydrogen in Titanium by Spectral Methods	328
7. Determination of Oxygen in Titanium in a Direct-Current Arc . . .	330
8. Determination of Oxygen in Titanium and Zirconium by the Isotope-Dilution Method	332
9. Spectral Determination of Hydrogen in Zirconium by the Isotope-Exchange Method	335
10. The Determination of Gases in Graphite, Silicon, Germanium, Tin, and Lead	336
Chapter XVI. DETERMINING GASES IN METALS OF THE FIFTH GROUP	341
1. The Determination of Gases in Vanadium	341
2. Determination of Gases in Niobium by the Vacuum-Fusion Method .	341
3. The Determination of Oxygen in Niobium by the Vacuum-Extraction Method	344

CONTENTS

4. The Determination of Gases in Tantalum by the Vacuum-Fusion Method	345
5. The Determination of Oxygen in Bismuth by the Hydrogen Method	346
6. The Determination of Oxygen in Antimony by the Hydrogen Method.	346
Chapter XVII. DETERMINING GASES IN METALS OF THE SIXTH AND SEVENTH GROUPS	347
1. A Review of Methods Used to Determine Gases in Metals of the Sixth Group	347
2. The Determination of Gases in Chromium by the Vacuum-Fusion Method	347
3. The Determination of Oxygen in Chromium by the Isotope-Dilution Method	350
4. The Determination of Hydrogen, Oxygen, and Nitrogen in Molybdenum and Tungsten by the Vacuum-Fusion Method.	350
5. The Determination of Gases in Manganese by the Vacuum-Fusion Method	352
Chapter XVIII. DETERMINING GASES IN METALS OF THE EIGHTH GROUP	353
1. A Review of Methods Used to Determine Gases in Steel	353
2. The Determination of Gases in Steel by the Vacuum-Fusion Method	354
3. The Determination of Gases in Steel by Spectral Methods.	357
4. The Determination of Oxygen in Iron by the Isotope-Dilution Method	361
5. The Determination of Gases in Cobalt, Nickel, and Platinum by the Vacuum-Fusion Method	361
Chapter XIX. THE DETERMINATION OF GASES IN LANTHANIDES AND ACTINIDES	363
1. The Determination of Gases in Lanthanum by the Vacuum-Fusion Method	363
2. The Determination of Gases in Thorium by the Vacuum-Fusion Method	366
3. The Determination of Gases in Uranium by the Vacuum-Fusion Method	367
Literature Cited	371

PART ONE

*THEORETICAL PRINCIPLES IN THE DETERMINATION
OF GASES IN METALS*

INTRODUCTION

Even the most "pure" metals contain small amounts of hydrogen, oxygen, and nitrogen. Regardless of the form in which they occur, these impurities are referred to as "gases in metals." Since these elements have an important effect on the physical and mechanical properties of metals their determination has received extensive development.

Due to the specific properties and quantities of the elements to be analyzed, the analysis of gases in metals has its special features. A metal always contains dissolved gases. These gases, however, are present not only in the form of a solution but also as disperse phases and in the adsorbed state.

Some idea of the presence of dissolved gases in various metals can be obtained from the data of Smithells [1], given in Table 1.

In the simplest case, when the hydrogen, oxygen, or nitrogen forms a true atomic solution in the metals, the partial pressure of the diatomic gas over the solution is proportional to the square of the concentration.

The analysis of gases in metals usually involves liberating the element either into the gaseous phase or in the form of a compound in the solid state. Gases are evolved from a metal by displacing the equilibrium so that they are removed from solution and the hydrides, oxides, and nitrides are dissociated.

For analytical purposes it is very important not only that the gases be completely evolved but that they suffer no losses in the apparatus. These losses can take place due to reaction of the gases with the material of the apparatus and with substances formed during the analysis. High losses usually occur as a result of adsorption of gases on sublimates formed by the evaporation of metals at the high temperatures needed for rapid and complete extraction of the gases. Furthermore, experimental errors can be caused by the gas collector of the apparatus, by the incorrect choice of a method for separating the gas mixture, and by several other factors.

In the removal of oxygen and nitrogen in the form of oxides and nitrides, difficulties are encountered in the selection of conditions for separating them from the metal without changing the amount of the element being analyzed.

Each method of analysis should provide the sensitivity and accuracy needed to evaluate the quality of the metal. For this reason, the development of methods for analyzing gases in metals is based on the laws of reaction between gases and metals and the degree of influence of gases on the properties of metals.

Table 1. The Solubility of Hydrogen, Nitrogen, and Oxygen in Metals

Group	Metals and metalloids	Solubility		
		H ₂	N ₂	O ₂
Ia	Li, Na, K, Rb, Cs	Form ionic hydrides, probably s	—	R O, probably i/s
Ib	Cu	s	i/s	Cu ₂ O, s
	Ag	s	i/s	Ag ₂ O, s
	Au	i/s	i/s	i/s
IIa	Be	Probably s/s	—	—
	Mg	s	—	—
	Ca, Sr, Ba	Form ionic hydrides RH ₂ , probably s	—	RO, probably s
IIb	Zn, Cd	Probably s/s	i/s	—
	Hg	i/s	i/s	i/s
IIIa	Sc, Y, Lanthanides	h/s → RH ₃	—	—
IIIb	B	Forms covalent hydrides RH ₃ , probably i/s	—	—
	Al	s	i/s ?	i/s
	Ga, In, Tl	i/s	—	—
IVa	Ti, Zr, Hf, Th	h/s → RH ₂ or RH ₃	h/s → RN or R ₃ N ₄	h/s
IVb	Si	Forms covalent hydrides SiH ₄ , probably i/s	—	—
	Ge	Forms covalent hydrides GeH ₄ , probably i/s	—	—
	Sn, Pb	s/s	i/s	SnO, PbO, s/s
Va	V, Nb, Ta	h/s → RH	h/s → RN	s/s
Vb	P, As, Sb, Bi	Forms covalent hydrides RH ₃	—	—
VIa	Cr, Mo, W	s/s	RN, probably s/s	—
	U	Forms the hydride UH ₃	s	—
VIIa	Mn	s	Mn ₃ N ₂ , s	—
VIIIa	Fe, Co, Ni	s	Soluble in Fe and Co	RO, s
	Ru, Rh, Pd	s	i/s	—
	Os, Ir, Pt	Soluble in Pt	i/s	i/s

Note: s-soluble; s/s-slightly soluble; h/s-highly soluble; i/s-insoluble.

CHAPTER I

THE HYDROGEN—METAL SYSTEM

1. The Thermal Stability of Hydrogen—Metal Systems

The liberation of hydrogen from metals in a vacuum usually presents no problems. At temperatures above 1000° all hydrides dissociate, and if the metal is in the molten state the most firmly bound part of the hydrogen is removed as well as the mobile part.

At the high temperatures reached in an electric arc or an electric discharge, molecular hydrogen dissociates into atoms. The energy of dissociation of molecular hydrogen is 103.4 kcal per mole of H_2 . An additional 312 kcal of energy per mole of H (13.53 ev per atom) is needed to ionize an atom of hydrogen. These facts are of interest for two reasons. In the first place, they indicate that hydrogen in metals is unlikely to exist only in the form of protons as stated by some workers [2], and in the second place, these facts should be borne in mind when selecting the light source for spectrographic analysis.

According to the classification proposed by Hurd [3] the elements of the first and second groups of the periodic system (Li, Na, K, Rb, Cs, Ca, Sr, Ba) form ionic hydrides which, in many respects, are analogs of the halides of these elements. The radius of the negative hydrogen ion in hydrides is much larger than the covalent radius of hydrogen. It can be assumed approximately that the thermal stability of compounds of elements with hydrogen, except for the hydrides of the transition metals, increases with increasing electronegativity of the elements. The hydrides of the transition metals are characterized by a reduction in the thermal stability with increase in the number of the group in the periodic system. The only stable compounds are those of hydrogen with the elements of groups III, IV, and V (Sc, Y, lanthanides, actinides, Ti, Zr, Hf, V, Nb, Ta). These elements have increased capacity for absorption of hydrogen, whereas the metals of group VIII, apart from palladium, are much less able to absorb hydrogen. In some cases the hydrogen compounds of the heavy elements are less stable than the hydrides of the light elements. The thermal effect of the reaction of tran-

sition metals with hydrogen consequently decreases in the periodic system from left to right (except chromium). The heats of formation of the hydrides of the transition metals of groups III and IV are of the same order as for the ionic hydrides.

The transition metals of groups VI, VII, and VIII form endothermic solutions with hydrogen.

Elements of the copper subgroup (Cu, Ag, Au), zinc subgroup (Zn, Cd, Hg), and also In and Tl form unstable intermediate hydrides. B, Al, Ga, and the elements of the carbon, nitrogen, oxygen, and halogen groups form covalent hydrides—volatile gases, and only in a few cases solids. The covalent hydrides are characterized by an increase in the thermal stability in a number of elements of the periodic system from left to right; for example, in the series Al, P, S, Cl the thermal stability increases. In the same group with increase in the atomic number the thermal stability of the covalent hydrides falls. In the group C, Si, Ge, Sn, Pb lead hydride is unstable even at room temperature.

The dissociation pressure of the hydrides is calculated from the standard free energy ΔZ° of the reaction $2Me_xH = 2xMe + (H_2)_{gas}$, according to the equation

$$\lg p_{H_2} \text{ mm Hg} = \frac{-\Delta Z^\circ}{4.575T} + 2.881. \quad (I-1)$$

Table 2 gives data on the temperature dependence of the dissociation pressure of certain hydrides.

In many metals most of the evolved hydrogen is taken from solution. In exothermic solutions, with increase in the temperature the solubility of the hydrogen decreases, and therefore heat alone liberates the hydrogen, as is immediately apparent from Table 3. In endothermic solutions, with increase in the temperature the solubility of hydrogen increases, the regularity being expressed by the following equation:

$$\frac{\lg S}{p^{1/4}} = -\frac{A}{T} + B, \quad (I-2)$$

where

S is the solubility of hydrogen in cubic centimeters per 100 g;

P is the pressure in millimeters of mercury;

T is the temperature in degrees Kelvin.

It is obvious that the direct extraction of hydrogen in this case is only possible at low pressures, as is shown by calculations using the data of Table 4. For the rapid extraction of hydrogen from an

* $\lg = \log_{10}$; $-\Delta Z^\circ = -\Delta G^\circ$; the Gibbs standard free energy.

Table 2. The Thermal Stability of Some Hydrides

No.	Formula	Conditions of thermal dissociation*	Remarks
1	LiH	$\lg p_{H_2} = -\frac{9337}{T} + 11.131$	At a temperature of 500° $p_{H_2} = 0.07$ mm Hg; at 680° it is 27 mm Hg; at 850° it is 760 mm Hg
2	NaH	$\lg p_{H_2} = -\frac{5700}{T} + 2.5 \lg T + 3.956$	Decomposes before melting; p_{H_2} at 425° equal to 1 atm
3	KH	$\lg p_{H_2} = -\frac{5850}{T} + 2.6 \lg T + 3.995$	At high temperatures the dissociation pressures of the hydride KH and the deuteride KD differ considerably
4	RbH	$\lg p_{H_2} = -\frac{4533.5}{T} + 9.20$	p_{H_2} at 320° is equal to 33.8 mm Hg
5	CsH	$\lg p_{H_2} = -\frac{3475.5}{T} + 7.50$	Partially dissociates in ultraviolet light ($\lambda = 2500$ to 3000 Å)
6	CaH ₂	$\lg p_{H_2} = -\frac{7782}{T} + 9.07$	In the presence of free metal the dissociation pressure decreases, for 85% CaH ₂ $\lg p = -\frac{10870}{T} + 11.493$
7	SrH ₂	Dissociation pressure somewhat higher than for calcium hydride	p_{H_2} depends on the content of free metal
8	BaH ₂	—	The dissociation pressure depends on the content of free metal
9	BeH ₂	—	Decomposes at 125°
10	MgH ₂	—	Start of decomposition 280–300°
11	Hydrides B, Al, Ga	Not encountered in monomer form Diborane B ₂ H ₆ decomposes at 300°; aluminum hydride decomposes to the elements at temperatures over 100°; digallane Ga ₂ H ₆ begins to decompose at 130°	
12	Hydrides C, Si, Ge, Sn, Pb	Methane CH ₄ exists in equilibrium with carbon and hydrogen at 1000°; monosilane begins to decompose at 400° and is fully decomposed at 600°; lead hydride is unstable even at room temperature	
13	AsH ₃	Decomposes when passed through a tube heated to 300°	
14	SbH ₃	Decomposes rapidly at 200°	